

HONDO ASPHALTENE DIFFUSION IN MICROPOROUS TRACK-ETCHED MEMBRANES

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1. ABSTRACT

The configurational diffusion of asphaltenes isolated from Hondo crude has been examined. Diffusion studies were performed with track-etched membranes with pore diameters in the range 100A to 4000A. The asphaltene is perceived as a lumped compound, containing a molecular weight range of heteroatomic species. The asphaltene does not diffuse as a single species, but may delaminate before diffusion. We report on the interesting phenomenon of the Hondo asphaltenes' vanadium fragments diffusing in 100A pores more rapidly, than the same asphaltenes' nickel fragments. This phenomenon is shown to be consistent with some previously reported conjectures on the relative distribution of nickel and vanadium within the asphaltene micelle.

2. INTRODUCTION

During the refining of heavy oils, contaminants such as nickel, vanadium and nitrogen must be catalytically removed from the oil. In hydroprocessing the nitrogen is reduced to ammonia, while the nickel and vanadium deposit as sulfides within the pores of the catalyst. Better HDM catalyst design mandates a greater understanding of the diffusion of an oil's metallorganics in the catalyst. Most HDM reactions are strongly diffusion limited at commercial process conditions as evidenced by the ringed nickel and vanadium intra-catalyst pellet metal profiles measured by electron microprobe.

A large fraction of a resid's heteroatoms are complexed in the solubility class called asphaltenes. Asphaltenes are polyaromatic sheet-like structures of large size and molecular weight.

In an attempt to mimic the diffusive transport of whole oil asphaltenes within a catalyst's pores, we have investigated the diffusion of an asphaltene, dissolved in pure xylene, through porous membranes with a range of pore sizes. Our results clearly indicate:

- The lumped compound nature of asphaltenes i.e. they are a solubility class, and as such are comprised of a spectrum of molecular types, each exhibiting a different diffusion coefficient.
- Hindered diffusion of asphaltenes is an important transport mechanism in resid upgrading catalysts.
- The asphaltene exclusion principle operates at low pore diameters.

3. EXPERIMENTAL

Asphaltene were isolated by n-pentane extraction from Hondo California crude oil. The crystalline like asphaltene powder was redissolved in xylenes to form a 5 weight percent asphaltene model feedstock. Diffusion experiments were conducted in a custom built stainless steel, agitated Wicke-Kallenbach type diffusion cell (1,2). The temperature was controlled at 45°C. The cell's two compartments were separated by polycarbonate membranes (PCM), whose pore size ranged from 100A to 4000A over the entire experimental sequence. The PCMs were purchased from from Nuclepore Corporation, Pleasanton, CA. PCMs are thought to simulate the porous structure of a catalyst, but in a highly idealized sense, since all tortuosity effects have been removed.

The experimental plan is outlined in Figure 1. The strategy was to use a single charge of the asphaltene solution in an experiment where the membrane pore diameter was initially held low i.e. at 100A. The batch-batch diffusion experiment was then monitored by removing samples for analysis from the low concentration (LC), initially pure xylene, side of the membrane.

After a predetermined time the experiment was temporarily suspended and the membrane changed to a larger pore diameter (in the sequence 150A, 300A and 4000A). Simultaneous with each membrane change the LC side has recharged with fresh xylene. The key point, however, is that the original asphaltene solution charge was carried through the entire experiment (Fig. 1), and permitted to lose asphaltene solute by successively recontacting it with pure xylene across increasing membrane pore diameters.

This experimental protocol permits us to examine the relative diffusion rates of the variously sized species which constitute an asphaltene.

Analysis of the LC side samples was performed by X-ray fluorescence for sulfur, nickel and vanadium, and by size exclusion chromatography (SEC) for molecular weight distributions. SEC data will be reported elsewhere.

4. RESULTS and DISCUSSION

The data from the diffusion of Hondo asphaltenes across the range of pore diameters (100-4000A) tested, is depicted in Figs 2 to 4. Sulfur, vanadium and nickel concentrations on the LC side of the membranes are shown as a function of time.

This raw data has been manipulated to generate Fig 5 where the relative initial slope for each species (S,V,Ni) at each pore diameter has been plotted. In addition, Fig 6 is an expanded view of the low time results for nickel and vanadium through the 100A membrane.

This data permits us to form the following evaluation:

- HINDERED TRANSPORT. By following the n-pentane asphaltene isolation procedure, we isolated an oil solubility class, comprised of a spectrum of molecular types and sizes. In this communication we infer little about asphaltene structure but note that it is an ongoing endeavor of our work to reconstruct asphaltene macrostructure from asphaltene diffusion studies. Figures 2 to 4 demonstrate the hindered nature of the transport of asphaltenes in a typical upgrading catalysts' sized pores. The data in these Figures also strongly suggests that small pores could exclude larger asphaltenic fragments.
- DISTRIBUTION OF HETEROATOMS IN ASPHALTENE FRAGMENTS. A semi-quantitative assessment of the data can be made from Fig. 5 which depicts initial slopes of the concentration versus time data as a function of membrane pore diameter.

With respect to each of the three diffusing asphaltene heteroatoms, sulfur, nickel, and vanadium we note:

-Sulfur appears evenly distributed among the various asphaltene sub-fragments, as evidenced by the almost proportional increase in initial transport rate with pore diameter.

-Nickel seems to be concentrated in species with sizes between 150A and 300A since the increase in relative transport rates between these pore diameters is a factor of 8, whereas the increase

between 300A and 4000A is only by a factor of 1.4.

-Vanadium seems to be concentrated with smaller fragments as indicated by the steady increase in vanadium transport rates only up to the 300A pore diameter.

- LOCATION OF METAL COMPOUNDS WITHIN HONDO ASPHALTENE MICELLE.

Figure 6 depicts our initial LC side data for nickel and vanadium diffusing in 100A pores. The interesting observation is that at low times vanadium species cross the membranes while nickel species are excluded. This finding has important implications in residuum hydroprocessing catalyst design. Perhaps vanadium could be selectively removed from the oil by judiciously engineering the catalyst pore size to exclude nickel fragments. The results of Fig. 6 suggest two things:

-The vanadium atoms are complexed in organometallic fragments which are physically smaller than the asphaltene's nickel fragments, or,

-Within the asphaltene micelle the vanadium species are more concentrated on the periphery of the asphaltene micelle, than the nickel species. As the asphaltene may "onion-skin delaminate" prior to diffusion, more rapid transport of the vanadium species would be expected.

The latter explanation is consistent with the work of Larson and Beuther (3) who, from reactivity studies, suggested that the vanadium to nickel ratio is higher on the edge of an asphaltene, than in the asphaltene core.

This demonstrates how it may be possible to infer some information on asphaltene structure from basic diffusivity data.

5. CONCLUSIONS

In summary, we have examined the diffusion of n-pentane isolated asphaltenes from Hondo crude across porous membranes containing molecularly sized pores (Fig. 1) and conclude:

- asphaltenes can be viewed as a lumped compound containing a range of molecular weights.
- diffusion is hindered, and depends strongly on the relative size of asphaltene fragment size and pore diameter. (Figs. 2 to 4)

- Sulfur, nickel, and vanadium heteroatoms may concentrate in different molecular size ranges. (Fig. 5)
- With 100A sized pores, initial diffusion data showed permeation of vanadium, but not nickel (Fig. 6). From this observation, we made some inferences on catalyst design and asphaltene structure.

6. REFERENCES

1. Sane, R. C., Webster, I.A., and Tsotsis, T. T. "A study of asphaltene diffusion through unimodal porous membranes", Paper No. 14f presented at AIChE Annual Meeting, New York, New York, November 1987. Paper available through the Engineering Societies Library, United Engineering Center, 345 East 47th Street, New York, NY 10017.
2. Sane, R. C., Webster, I. A. and Tsotsis, T. T. in "Catalysis, 1987", Proc. 10th North American Meeting of the Catalysis Society, J. W. Ward (Editor), May 1987, San Diego, California, Pub. Elsevier, 1988.
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FIGURE 1
EXPERIMENTAL SEQUENCE

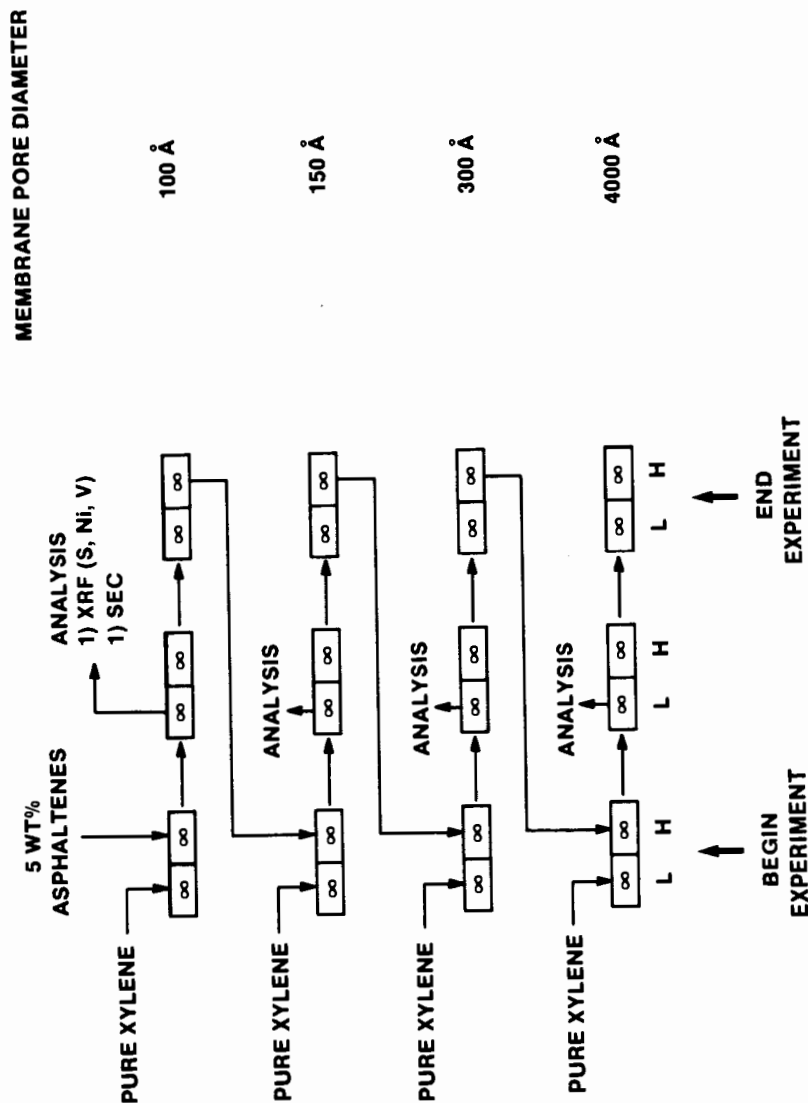


FIGURE 2: Low concentration side sulfur concentrations

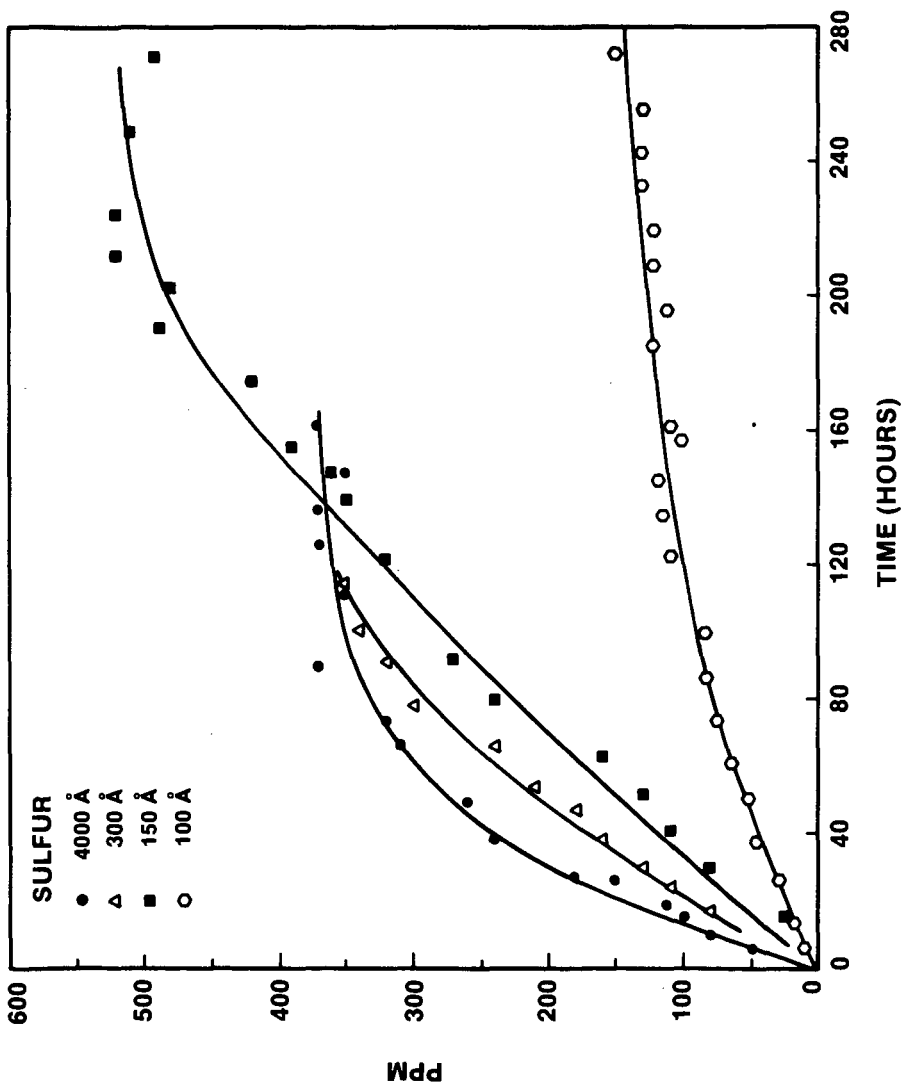


FIGURE 3: Low concentration side vanadium concentrations

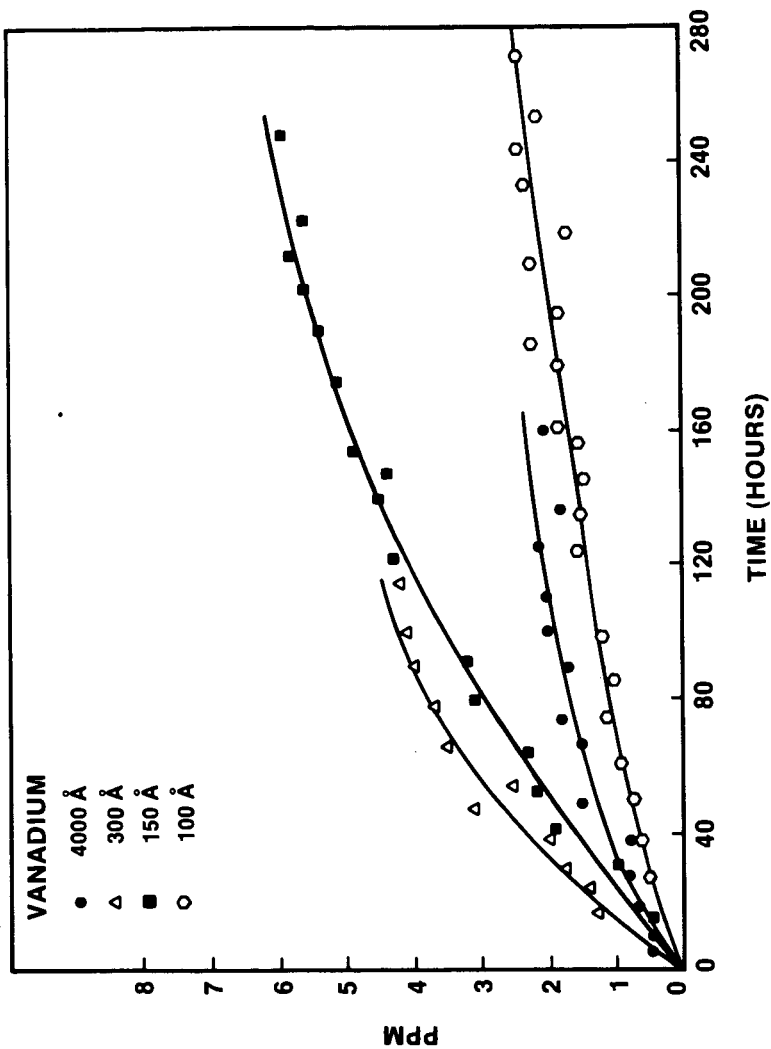


FIGURE 4: Low concentration side nickel concentrations

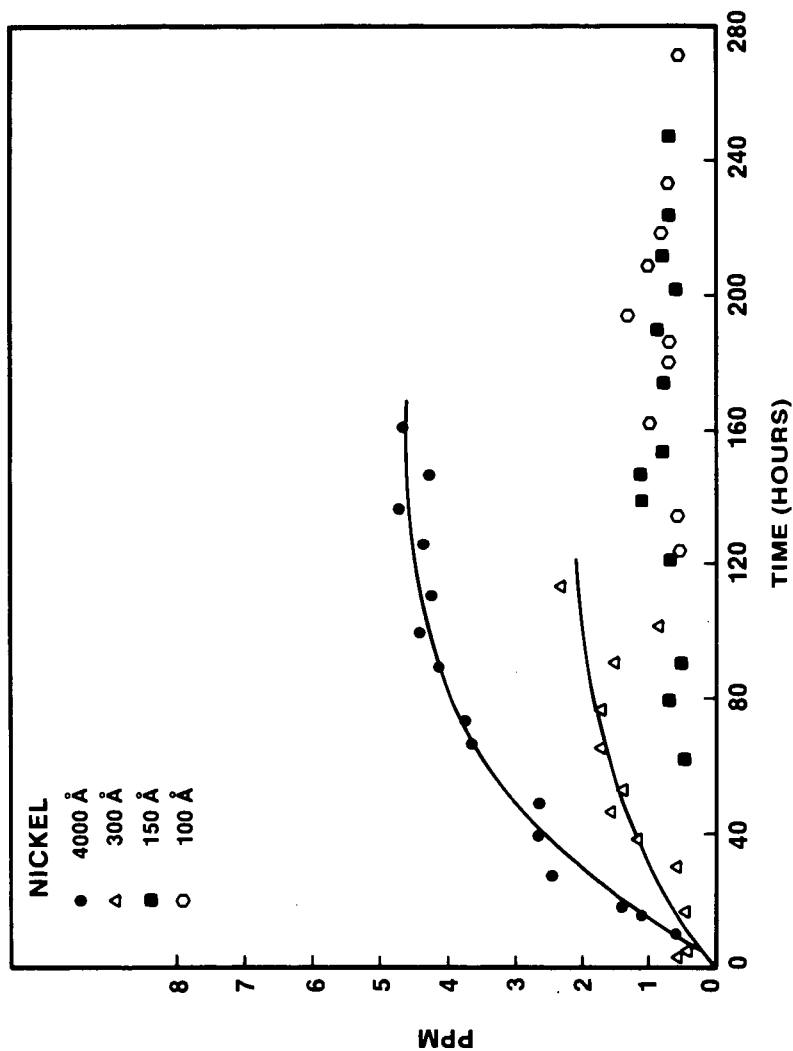


FIGURE 5
RELATIVE INITIAL TRANSPORT RATES (PPM/HOUR)

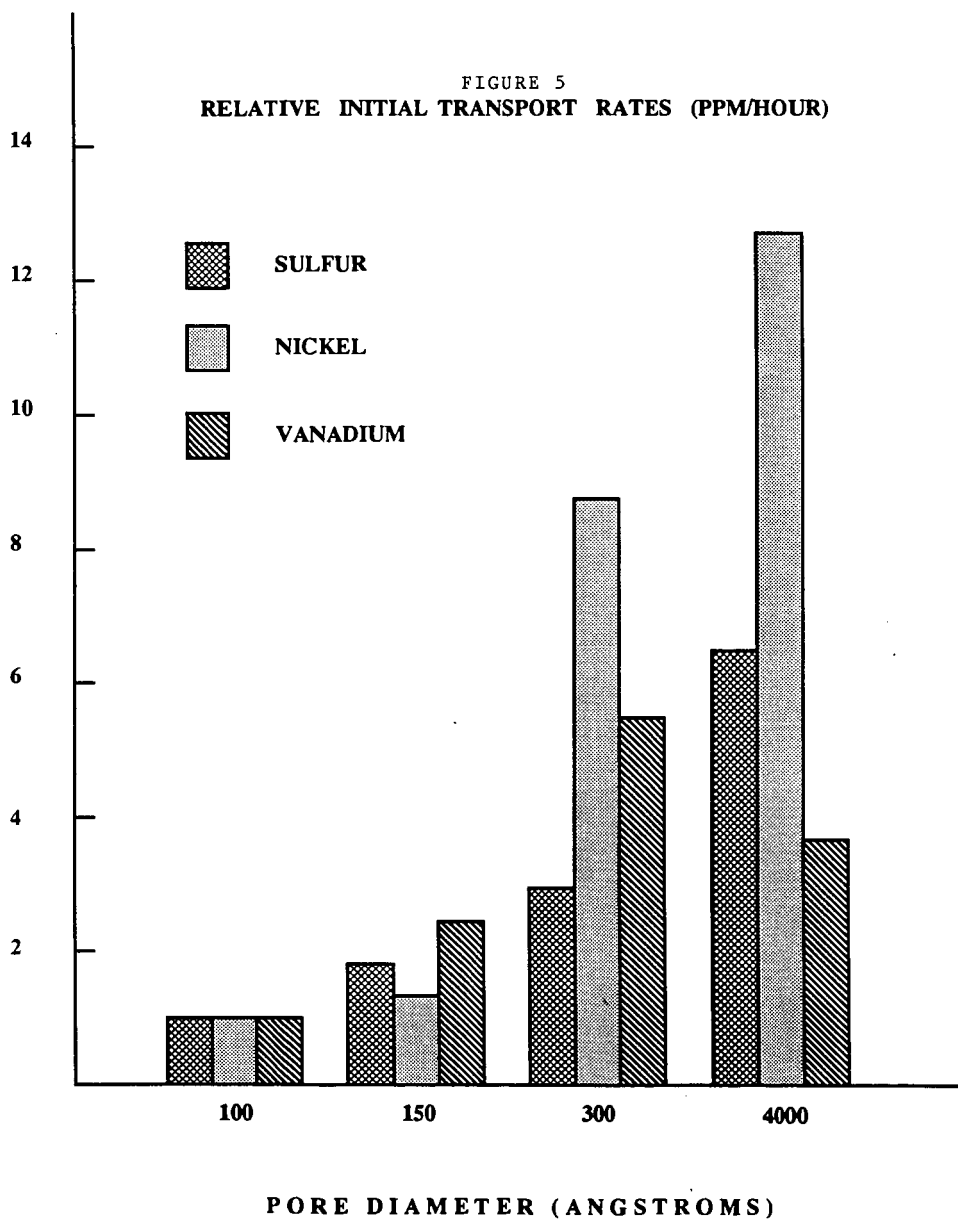


FIGURE 6: Low concentration side nickel and vanadium concentrations for 100A pore diameter membrane

